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Abstract: We present preliminary results from large scale molecular dynamics (MD) simulations of homogenous vapor to liquid nucleation. The simulations contain between one and eight billion Lennard-Jones atoms and were run for up to 56 million time-steps. The large particle numbers (over 104 times larger than previous simulations, see e.g. [2]) have several advantages: i) Resolving and quantifying nucleation at low supersaturations becomes possible within an accessible number of simulation time-steps, in spite of the very slow nucleation. ii) Even after forming many stable droplets the depletion of the vapor phase is negligible, i.e. the supersaturation remains constant during the simulations. iii) Excellent statistics on liquid droplet abundances and microscopic properties over a wide range in droplet sizes. iv) Simulations can be run efficiently on a large number of cpus. First, direct comparisons to laboratory experiments[6] are now possible: we find excellent agreement in the nucleation rates at kT = 0.3 and somewhat lower rates in the simulations at kT = 0.4 . At low temperatures, modified classical nucleation theory significantly underestimates the nucleation rates (by up to 109) and at kT = 1.0 it overestimates the nucleation rates by up to 105. The semi-phenomenological model[3] matches the nucleation rates and the cluster size distributions found in previous MD simulations at higher supersaturations quite well[2]. But at the lower supersaturations probed here, its predictions differ from the MD results by large factors (up to 103.5). We will also present MD results on cluster size distributions, free energy functions, sticking probabilities and condensation and evaporation rates. The microscopic properties (shapes, density profiles, binding energies, etc.) of the large numbers of droplets formed are presented in a separate contribution to this conference (Angélil et. al).

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Large Scale MD Simulations of Nucleation

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Abstract. We present preliminary results from large scale molecular dynamics (MD) simulations of homogenous vapor to liquid nucleation. The simulations contain between one and eight billion Lennard-Jones atoms and were run for up to 56 million time-steps. The large particle numbers (over 10^4 times larger than previous simulations, see e.g. [2]) have several advantages: i) Resolving and quantifying nucleation at low supersaturations becomes possible within an accessible number of simulation time-steps, in spite of the very slow nucleation. ii) Even after forming many stable droplets the depletion of the vapor phase is negligible, i.e. the supersaturation remains constant during the simulations. iii) Excellent statistics on liquid droplet abundances and microscopic properties over a wide range in droplet sizes. iv) Simulations can be run efficiently on a large number of cpus.

First, direct comparisons to laboratory experiments[6] are now possible: we find excellent agreement in the nucleation rates at $kT = 0.3\varepsilon$ and somewhat lower rates in the simulations at $kT = 0.4\varepsilon$.

At low temperatures, modified classical nucleation theory significantly underestimates the nucleation rates (by up to 10^9) and at $kT = 1.0\varepsilon$ it overestimates the nucleation rates by up to 10^5. The semi-phenomenological model[3] matches the nucleation rates and the cluster size distributions found in previous MD simulations at higher supersaturations quite well[2]. But at the lower supersaturations probed here, its predictions differ from the MD results by large factors (up to $10^{3.5}$).

We will also present MD results on cluster size distributions, free energy functions, sticking probabilities and condensation and evaporation rates. The microscopic properties (shapes, density profiles, binding energies, etc.) of the large numbers of droplets formed are presented in a separate contribution to this conference (Angélil et. al).

Keywords: drops, equations of state, Lennard-Jones potential, molecular dynamics method, nucleation, solid-vapour transformations
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INTRODUCTION AND THEORETICAL MODELS

Molecular dynamics (MD) simulations are able to directly resolve details of the nucleation process and they provide useful test cases for nucleation models, see e.g. [1, 2] and references therein. The free energy ΔG_i associated with forming a liquid cluster of size i from the vapor phase has a positive surface term, corresponding to the work required to form the vapor-liquid interface, and a volume term which is negative for supersaturated vapor. ΔG_i reaches a maximum at a critical cluster size, i^*. Larger clusters are considered to be stable and smaller ones unstable. The equilibrium number density of small, unstable clusters is

$$n_e(i) = \frac{P_1}{kT} \exp\left[-\frac{\Delta G_i}{kT}\right] , \quad (1)$$

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where P_1 is the monomer pressure. Stable clusters grow predominantly by accreting monomers (the most abundant species). The transition rate from i-mer to $(i+1)$-mer is

$$R^+(i) = \alpha n_e(1) v_{th}\, 4\pi r_0^2 i^{2/3}\,, \tag{2}$$

where α is the sticking probability and v_th is the mean thermal velocity. r_0 is the mean inter-particle separation in the liquid phase, therefore $4\pi r_0^2 i^{2/3}$ corresponds to the surface area of an i-mer. The nucleation rate J is approximately proportional to the abundance of critical clusters and their transition rate times the Zeldovich factor Z (see e.g. [4, 2]):

$$J = \left[\sum_{i=1}^{\infty} \frac{1}{R^+(i) n_e(i)}\right]^{-1} \simeq R^+(i^*) n_e(i^*) Z\,. \tag{3}$$

In the (modified) classical nucleation theory (CNT and MCNT)[4] and in the semi-phenomenological (SP) model[3], the free energies ΔG_i are chosen to be

$$\Delta G_{i,\mathrm{CNT}}/kT = -i\ln S + \eta i^{2/3} \tag{4}$$

$$\Delta G_{i,\mathrm{MCNT}}/kT = -(i-1)\ln S + \eta(i^{2/3}-1) \tag{5}$$

$$\Delta G_{i,\mathrm{SP}}/kT = -(i-1)\ln S + \eta(i^{2/3}-1) + \xi(i^{1/3}-1)\,, \tag{6}$$

where $S = P_1/P_{\mathrm{sat}}$ is the supersaturation ratio and $\eta = 4\pi r_0^2\gamma/kT$ relates to the surface tension γ. The parameter ξ is fixed by using the second virial coefficient.

NUMERICAL SIMULATIONS

The MD simulations were performed with the LAMMPS code[5] on up to 32'768 cpus on the HERMIT and SuperMUC supercomputers. We use the Lennard-Jones potential $u(r)/4\varepsilon = (\sigma/r)^{12} - (\sigma/r)^6$ with a cutoff at 5σ. The simulated volumes are periodic cubes and the average temperature was fixed by rescaling velocities at every time-step. The time-steps are set to $\Delta t = 0.01\tau = 0.01\sigma\sqrt{(m/\varepsilon)}$. In the argon system the units are $\varepsilon/k = 119.8K$, $\sigma = 3.405$ Å, $m = 6.634\times10^{-23}g$ and $\tau = 2.16ps$.

The simulations contain one to eight billion particles, which is a large increase over previous simulations of this kind.This allows us to resolve nucleation at lower supersaturations and therefore much lower nucleation rates. Liquid clusters were identified on the fly and written out many times during each run using the definition from [1, 2]. The first results described here are all based on these cluster counts. The simulations also provide more detailed, microscopic information about the liquid clusters (e.g. their accretion and evaporation rates, density profiles, shapes, binding energies, etc.) and excellent statistics over a wide range of cluster sizes thanks to the large particle number (see Angélil et al., in these proceedings).

FIRST, PRELIMINARY RESULTS

Nucleation rates are derived form the growth rate of the number of clusters above some size threshold (e.g. larger than 70 particle in the example shown on the top left of

TABLE 1. Simulation properties: temperature T, number of particles N, periodic cube size L, initial monomer number density, total run time and initial supersaturation $S_{t=0}$.

Run ID	T [ε/k]	N	L[σ]	$\mathbf{n(1)_{t=0}}$ [σ^{-3}]	$\mathbf{t_{end}}$ [τ]	$\mathbf{S_{t=0}}$
T10n6	1.0	10^9	2554.4	6.00×10^{-2}	2.55×10^{3}	2.36
T10n58	1.0	10^9	2583.4	5.80×10^{-2}	9.33×10^{3}	2.28
T10n55	1.0	10^9	2629.5	5.50×10^{-2}	2.37×10^{4}	2.16
T8n25	0.8	10^9	3420.0	2.50×10^{-2}	4.03×10^{3}	4.42
T8n3	0.8	10^9	3218.3	3.00×10^{-2}	3.98×10^{3}	5.30
T8n2	0.8	10^9	3684.0	2.00×10^{-2}	1.13×10^{5}	3.53
T6n8	0.6	10^9	5000.0	8.00×10^{-3}	5.00×10^{3}	18.9
T6n65	0.6	10^9	5358.3	6.50×10^{-3}	3.00×10^{4}	15.3
T6n55	0.6	10^9	5848.0	5.00×10^{-3}	1.81×10^{5}	11.8
T4n10	0.4	10^9	10000	1.00×10^{-3}	3.95×10^{4}	498
T4n7	0.4	10^9	11263	0.70×10^{-3}	2.85×10^{5}	349
T4n6	0.4	8×10^9	23713	0.60×10^{-3}	2.70×10^{4}	299
T4n5	0.4	10^9	12599	0.50×10^{-3}	5.61×10^{5}	249
T3n14	0.3	10^9	19259	1.40×10^{-4}	1.55×10^{5}	1.66×10^{4}
T3n12	0.3	10^9	20274	1.20×10^{-4}	1.90×10^{5}	1.42×10^{4}
T3n9	0.3	10^9	22314	0.90×10^{-4}	3.75×10^{5}	1.07×10^{4}

Figure 1), after some initial lag time (vertical dashed lines). The rates are found to be independent of size threshold as long as the threshold is larger than i^*. Four low density runs did not produce a significant number of stable clusters and only allow to set upper limits on J (downward arrows, top right panel).

Model predictions for J often differ form the measured rates J_{MD} by many orders of magnitude, especially for the classical models, CNT and MCNT. The SP model on the other hand successfully matches the results from previous, smaller MD simulations at higher S and J [1, 2]. But in the lower S and J (and therefore larger i^*) regime probed here, the deviations from the SP model become quite large: J_{SP}/J_{MD} exceeds 10^3 in some cases. These limitations of the models also result in deviations in their predictions for the equilibrium abundances of small clusters (Eqn. 1).

The lower right panel in Figure 1 shows the sticking probabilities α derived from the growth rate of the largest cluster in each simulation (as in [2]). The sticking probabilities lie in a range from $\alpha = 0.05$ to 0.21 in our MD simulations, and they continue on the trend of decreasing α for decreasing S found in[2]. The model predictions in the bottom left panel assume $\alpha = 1$, as usual. Using the measured α values instead would lower the J_{model} values, but not enough to make the SP model fit the measured J_{MD} values.

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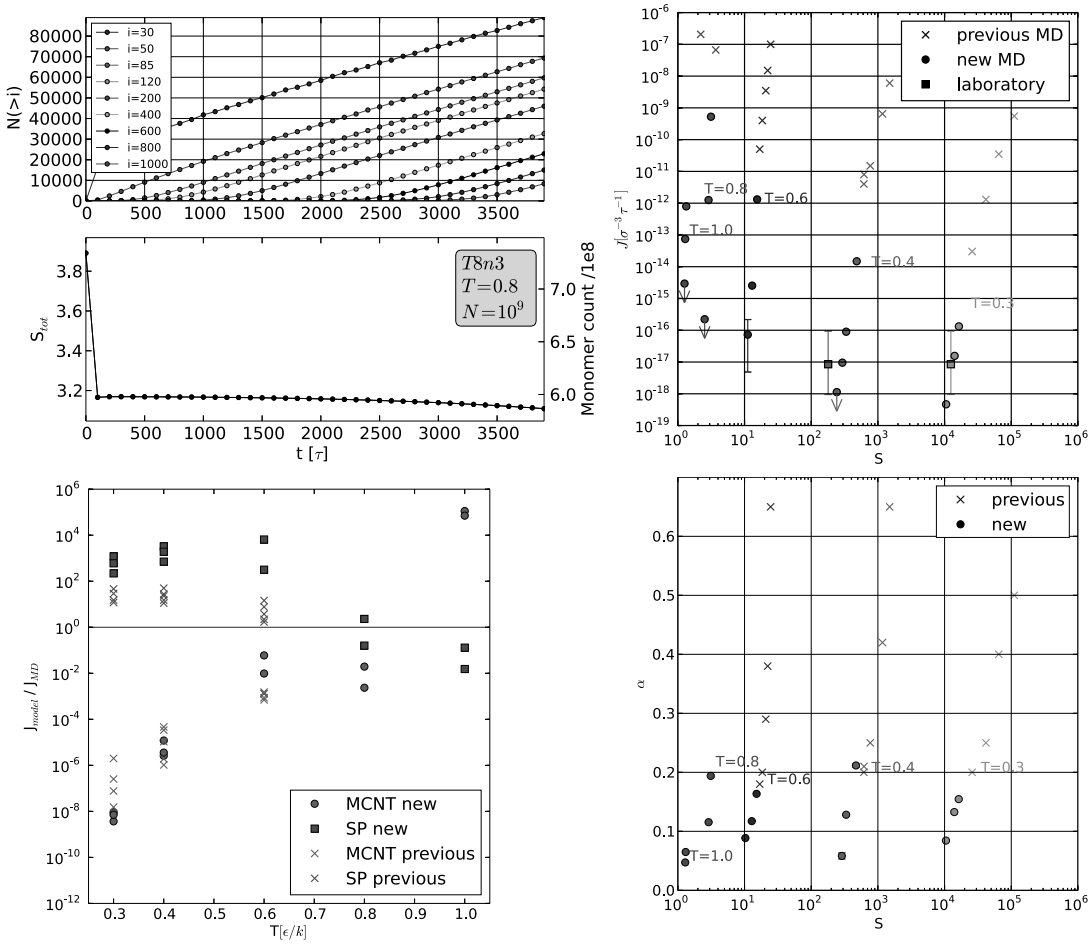

FIGURE 1. Top left: Number of clusters with more i atoms vs. time, for a range of threshold sizes i, and evolution of the monomer count and S. Top right: Overview of nucleations rates from our runs and from [1, 2] and experimental results from [6]. Bottom left: Comparison of measured nucleation rates and model predictions. Bottom right: sticking probabilities from our runs and from [2].

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